

PROCESS FOR PRODUCING HALOGENATED
AROMATIC AMINE COMPOUND

BACKGROUND OF THE INVENTION

5 Field of the Invention

This invention relates to a process for producing a halogenated aromatic amine compound.

Related Background Art

Halogenated aromatic amine compounds are useful
10 compounds as intermediates of pharmaceuticals and agricultural chemicals, intermediates of coloring matters such as organic dyes and pigments, and also intermediates of organoelectroluminescence materials, and intermediates of photosensitive materials or
15 organic conductor materials of organic photosensitive members in electrophotography.

In synthesizing halogenated aromatic amine compounds by conventional processes, they have been synthesized by, e.g., in the case of aminobiphenyl
20 compounds, the reaction in which an aminobiphenyl compound is directly halogenated, or the Ullmann reaction in which a dihalogenated biphenyl compound and an amine compound are heated at a high temperature in the presence of a copper reagent (DAIYUHKI KAGAKU
25 (Grand Organic Chemistry), Vol. 16, 52(1959), Asakura Shoten; YUHKIKAGAKU KOZA (Organic-Chemistry Course) 3, 66 (1983)). However, in the reaction in which an

aminobiphenyl compound is directly halogenated, an isomer different in halogen substitution position is present, and hence the desired compound can not efficiently be obtained. In the Ullmann reaction as well, the reaction has no selectivity, and hence not only the desired halogenated aminobiphenyl compound but also a diaminobiphenyl compound are simultaneously formed to make it unable to obtain the desired compound efficiently. Accordingly, it has been sought to provide a process for producing halogenated aromatic amine compounds efficiently.

Recently, a method developed by Buchwald or Hartwig et al. is also reported in which an arylhalide compound and an amine compound are allowed to react in the presence of a palladium catalyst to synthesize an arylamine compound efficiently (Tetrahedron Letters, Vol.36, No.21, p.3609, 1995; J. Am. Chem. Soc., Vol.120, p.9772, 1998; J. Or. Chem., 61, p.1133, 1996). Syntheses in which this reaction is applied to the syntheses of dihalogenated biphenyl compounds are disclosed in Japanese Patent Applications Laid-open No. 11-21349 and No. 11-322679. In either of them, however, all halogen moieties of a dihalogenated biphenyl compound are aminated, and there is shown no example of synthesizing halogenated aminobiphenyl compounds.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing a specific halogenated aromatic amine compound in a high selectivity and a high yield.

5 The present inventors have made extensive studies to settle the above subject. As the result, they have accomplished the present invention.

 The present invention is a process for producing a halogenated aromatic amine compound, comprising
10 allowing an aromatic amine compound represented by the following Formula (1):



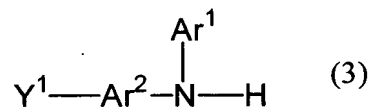
 wherein Ar^1 represents a substituted or unsubstituted monovalent aromatic hydrocarbon ring group or a
15 substituted or unsubstituted monovalent aromatic heterocyclic ring group;

 to react with a dihalogenated aromatic compound represented by the following Formula (2):



20 wherein Ar^2 represents a substituted or unsubstituted divalent aromatic hydrocarbon ring group or a substituted or unsubstituted divalent aromatic heterocyclic ring group, and Y^1 and Y^2 each independently represent an iodine atom, a bromine atom
25 or a chlorine atom;
 in the presence of a metallic catalyst and a basic compound in a non-reactive solvent to obtain a

halogenated aromatic amine compound represented by the following Formula (3):

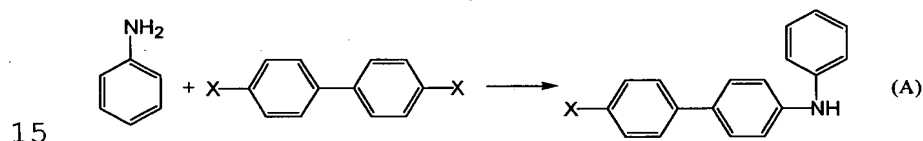


wherein Ar¹, Ar² and Y¹ are as defined above;

- 5 the metallic catalyst being a catalyst having a phosphorus-containing ligand having at least one cyclic hydrocarbon group.

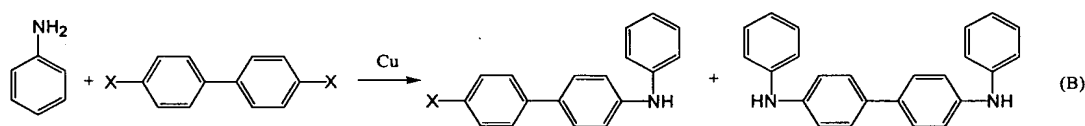
DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 10 Where the halogenated aminobiphenyl compound is synthesized by the production process of the present invention, the desired compound is selectively obtained as shown by the following reaction scheme (A):



wherein X represents an iodine atom, a bromine atom or a chlorine atom.

- However, where the compound is synthesized by the Ullmann process, not only the desired product is obtained, but also a product on both sides of the biphenyl of which have been aminated is obtained as a by-product, as shown by the following reaction scheme (B):
- 20



The reason why such a product on both sides of the biphenyl of which have been aminated is obtained has not been elucidated in detail, and it is presumed to be due to the fact that the Ullmann reaction requires high temperature (about 200°C) and this makes the reaction have a low selectivity.

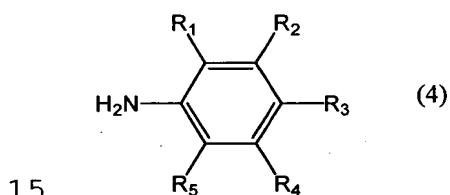
Where the halogenated aminobiphenyl compound is synthesized by the method developed by Buchwald or Hartwig et al. in which an arylamine compound is synthesized in the presence of a palladium catalyst and using tri(tert-butyl)phosphine disclosed in Japanese Patent Applications Laid-open No. 11-21349 and No. 11-322679, not only the desired product is obtained but also a product on both sides of the biphenyl of which have been aminated is obtained as a by-product. The reason therefor has not been elucidated in detail, and it is presumed to be due to the fact that the palladium catalyst and a metallic catalyst formed from the tri(tert-butyl)phosphine have so high reactivity that the selectivity of reaction has lowered, so that the product on both sides of the biphenyl of which have been aminated is obtained.

In the present invention, the aromatic amine compound represented by Formula (1) is allowed to react with the dihalogenated aromatic compound

represented by Formula (2) in the presence of i) a metallic catalyst having a phosphorus-containing ligand having at least one cyclic hydrocarbon group and ii) a basic compound in a non-reactive solvent to
5 produce the halogenated aromatic amine compound represented by Formula (3). The high selectivity brought out by this process has not been elucidated in detail, but the following reasons may be given therefor. In the production process in the present
10 invention, the reaction does not require so high temperature as that required in the Ullmann process, and hence this does not lower the selectivity of reaction. Also, the synthesis method developed by Buchwald or Hartwig et al. requires a ligand which
15 feeds electric charges to the metallic catalyst. Thus, the flow of electric charges from the ligand into the metal is so large that the metallic catalyst may come to have electric charges in a high density, whereupon the oxidative addition reaction of an aromatic
20 carbon/halogen bond on the metal, which corresponds to the first step of a catalyst cycle, is restrained when an electron-donative group is present on the aromatic group, as so presumed. It is considered that, at the stage where the halogen atom on one side of the
25 dihalogenated aromatic compound has been aminated, the density of electric charges between the other halogen and the carbon is so high that the both-side halogen

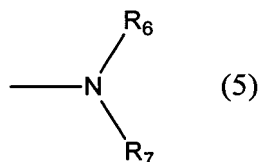
atoms are inhibited from being aminated together, and the selectivity is brought out such that only the halogen atom on one side is aminated. It, however, is considered that, where a trialkylphosphine, in which
5 all the hydrogen atoms on the phosphorus have been substituted with alkyl groups, is used as a ligand of the metallic catalyst, the flow of electric charges into the central metal is so large as to make the rate of reaction very high to cause a lowering of
10 selectivity.

In the present invention, the aromatic amine compound represented by Formula (1) may preferably be an aromatic amine compound represented by the following Formula (4):



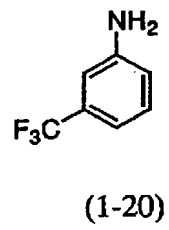
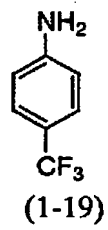
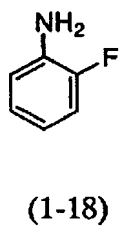
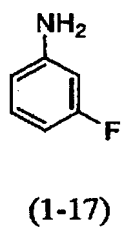
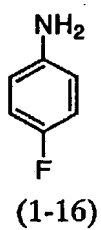
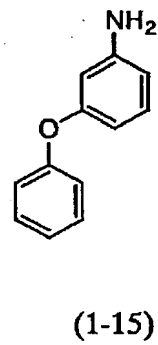
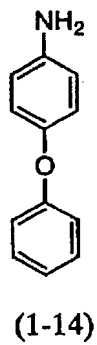
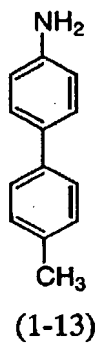
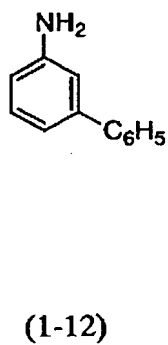
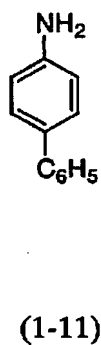
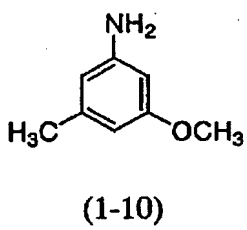
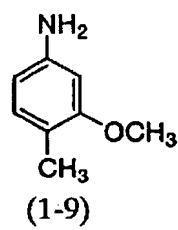
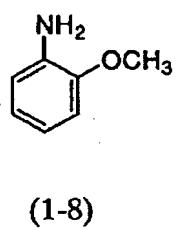
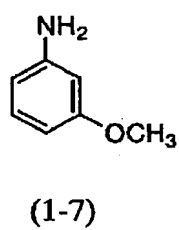
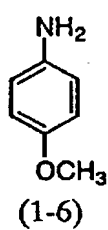
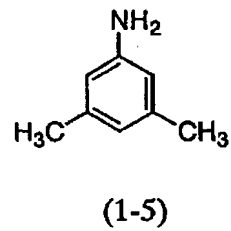
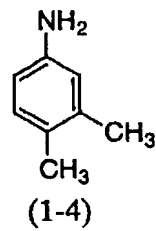
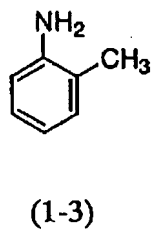
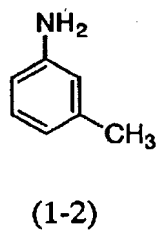
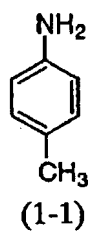
wherein R₁ to R₅ each independently represent a hydrogen atom, a substituted or unsubstituted alkyl group having any of 1 to 8 carbon atoms, a substituted or unsubstituted alkoxyl group having any of 1 to 8
20 carbon atoms, a substituted or unsubstituted aryl group, a substituted or unsubstituted aryl ether group, a fluorine atom, an alkyl fluoride group having any of 1 to 8 carbon atoms, a substituted or unsubstituted aryl thioether group, a substituted or unsubstituted

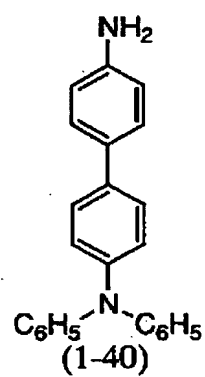
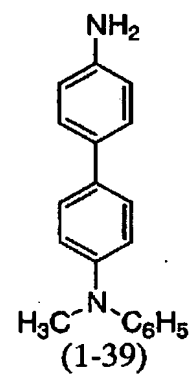
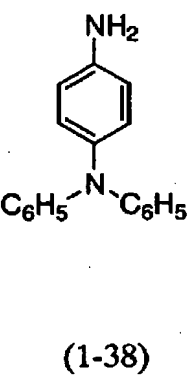
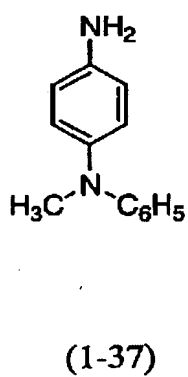
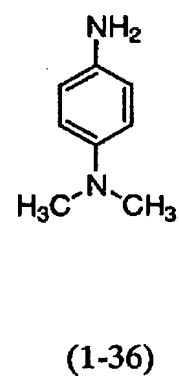
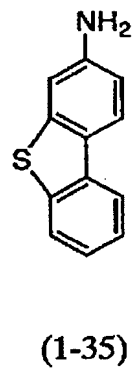
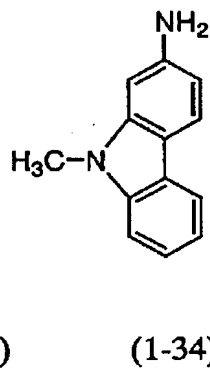
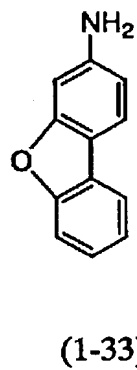
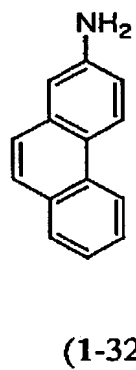
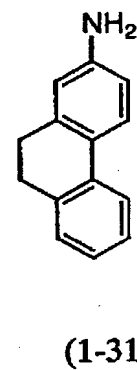
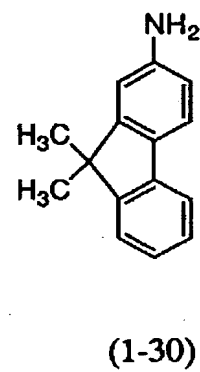
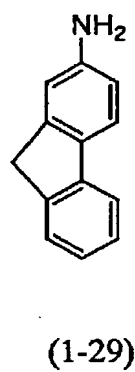
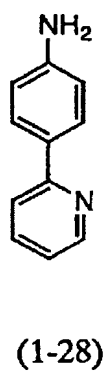
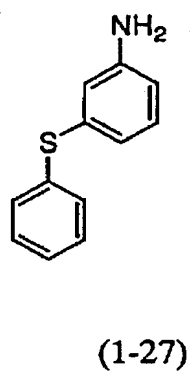
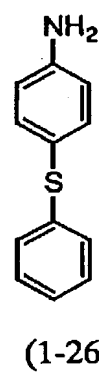
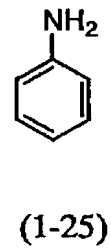
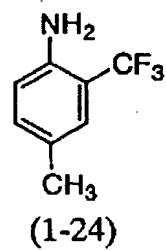
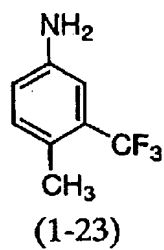
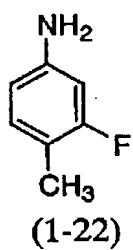
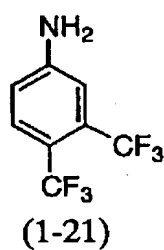
pyridyl group, or a group represented by the following
Formula (5):

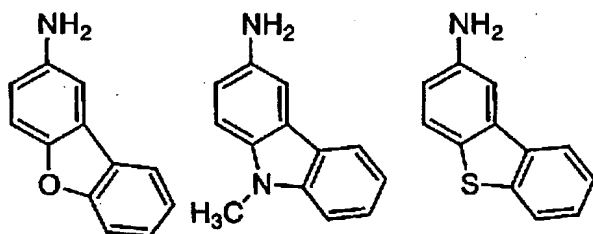


wherein R₆ and R₇ each independently represent a
5 substituted or unsubstituted alkyl group or a
substituted or unsubstituted aryl group.

Specific structural examples of the aromatic
amine compound represented by Formula (1) in the
present invention are shown below, but not
10 particularly limited to these structures.





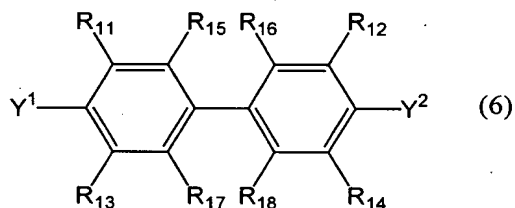


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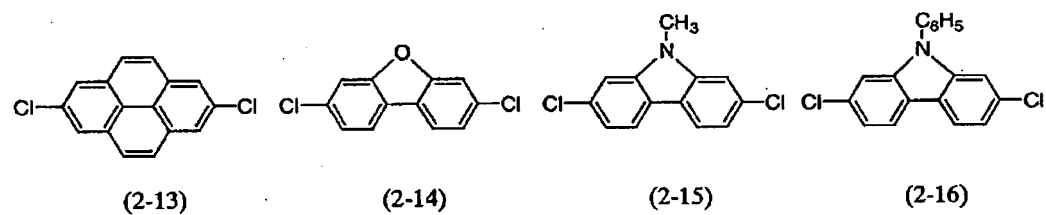
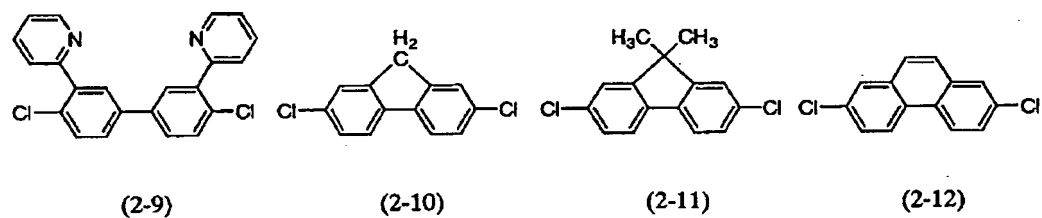
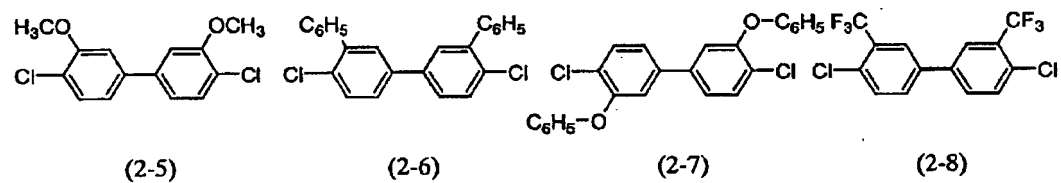
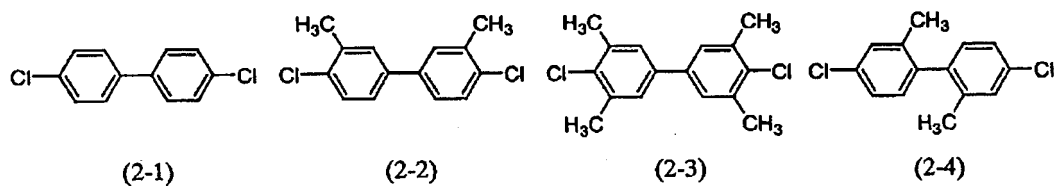
In the present invention, the dihalogenated aromatic compound represented by Formula (2) may preferably be a dihalogenated aromatic compound
5 represented by the following Formula (6):

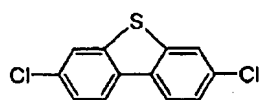


wherein R_{11} to R_{18} each independently represent a hydrogen atom, a substituted or unsubstituted alkyl group having any of 1 to 8 carbon atoms, a substituted or unsubstituted alkoxy group having any of 1 to 8 carbon atoms, a substituted or unsubstituted aryl group, a substituted or unsubstituted aryl ether group, an alkyl fluoride group having any of 1 to 8 carbon atoms, a substituted or unsubstituted aryl thioether group or a substituted or unsubstituted pyridyl group;
15 R_{15} and R_{16} , and R_{17} and R_{18} , may respectively independently combine through a carbon atom, a substituted or unsubstituted alkylene group, a

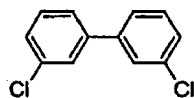
substituted or unsubstituted alkylidene group, an oxygen atom, a nitrogen atom or a sulfur atom to form a condensed polycyclic structure or a heterocyclic structure; and Y^1 and Y^2 each independently represent
5 an iodine atom, a bromine atom or a chlorine atom. The Y^1 and Y^2 in Formula (2) may also each preferably be a bromine atom.

Specific structural examples of the dihalogenated aromatic compound represented by Formula (2) in the
10 present invention are shown below, but not particularly limited to these.

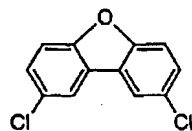




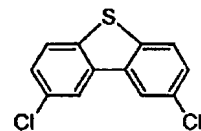
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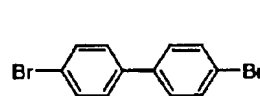
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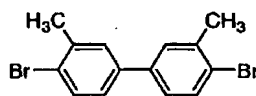
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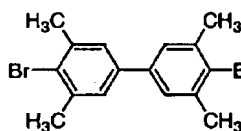
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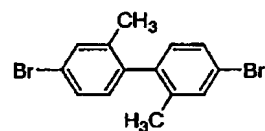
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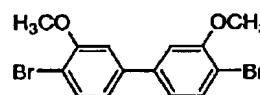
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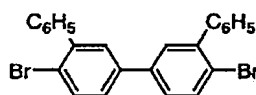
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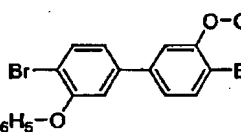
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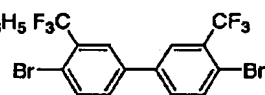
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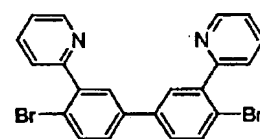
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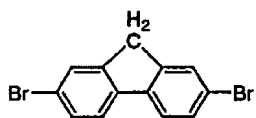
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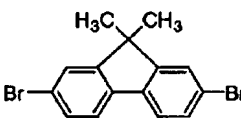
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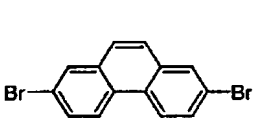
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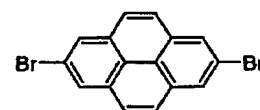
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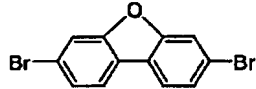
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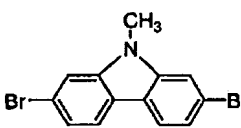
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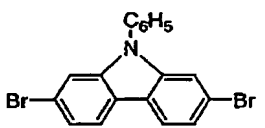
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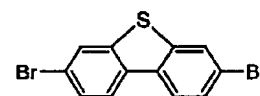
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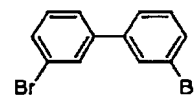
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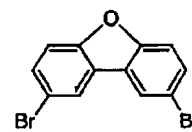
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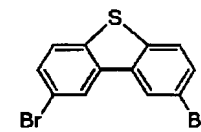
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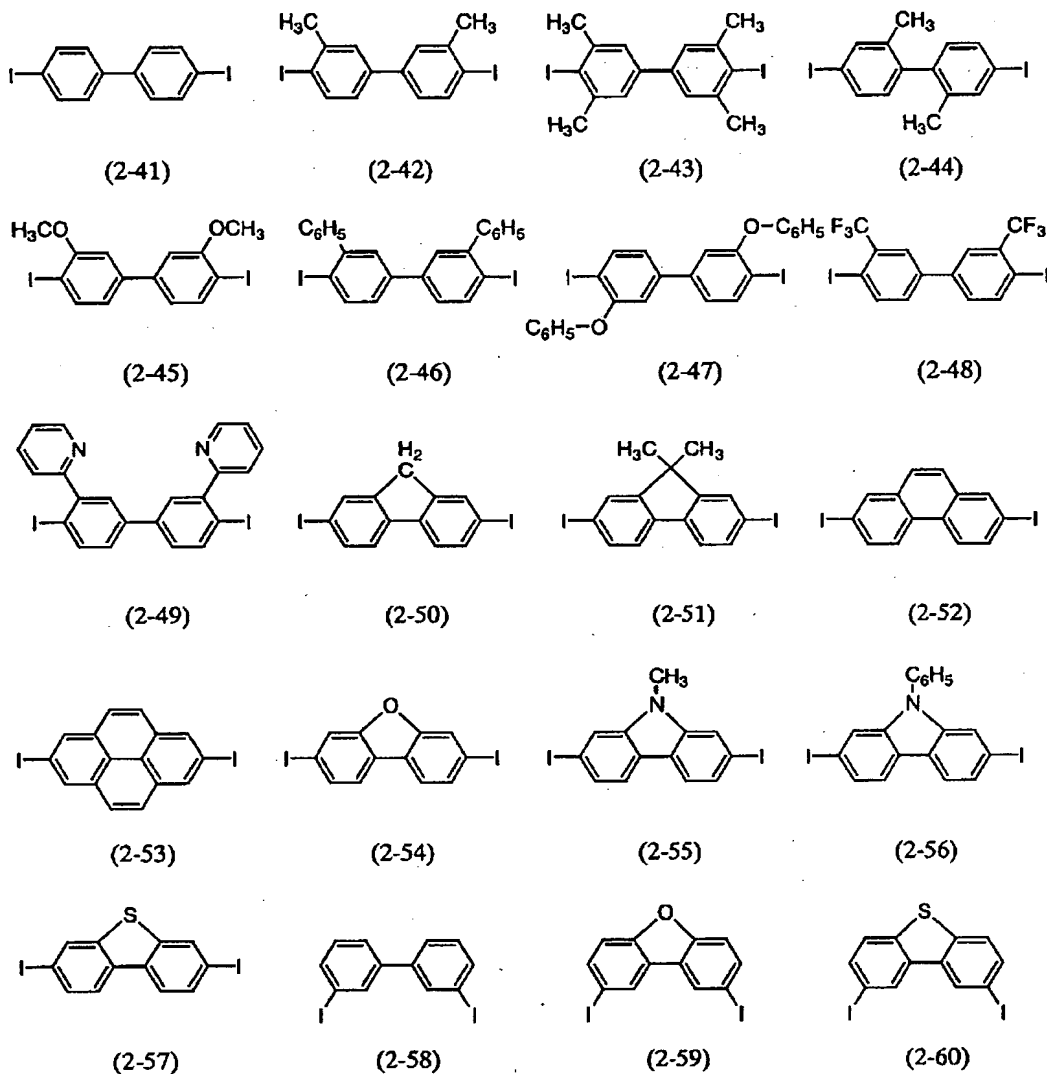
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(2-39)



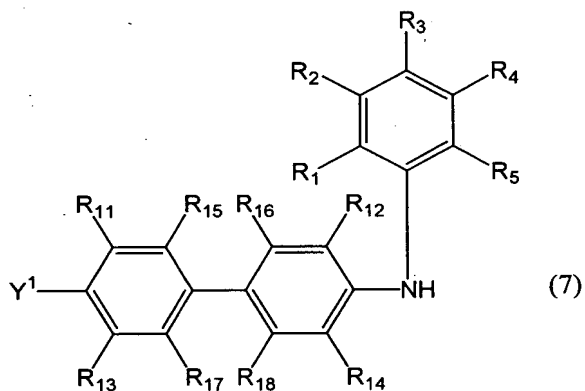
(2-40)



The dihalogenated aromatic compound represented by Formula (2) may preferably be used in an amount of from 1.0 time to 1.2 times in number of moles, based on the aromatic amine compound represented by Formula (1). It may more preferably be used in an amount of from 1.0 time to 1.1 times based on the aromatic amine compound represented by Formula (1).

In the present invention, the halogenated

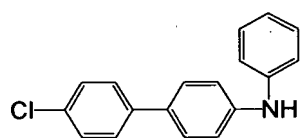
aromatic amine compound represented by Formula (3) may preferably be a halogenated aromatic amine compound represented by the following Formula (7):



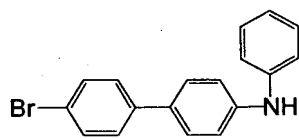
5 wherein R₁ to R₅, R₁₁ to R₁₈ and Y¹ are as defined previously.

Specific structural examples of the halogenated aromatic amine compound represented by Formula (3) in the present invention are shown below, but not particularly limited to these.

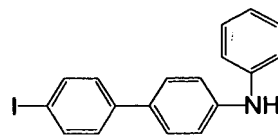
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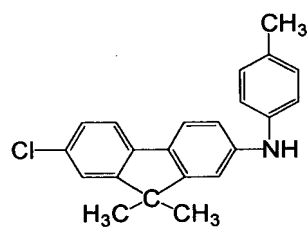
(3-1)



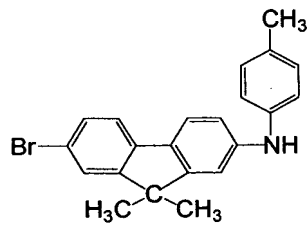
(3-2)



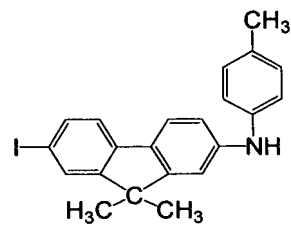
(3-3)



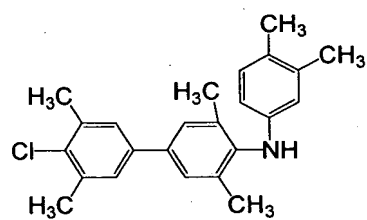
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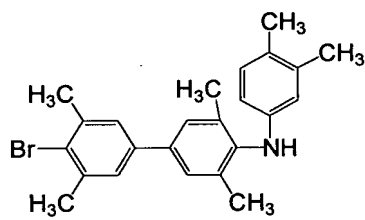
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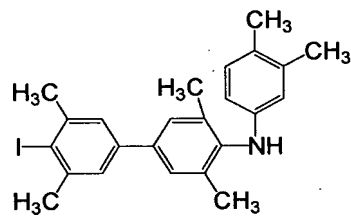
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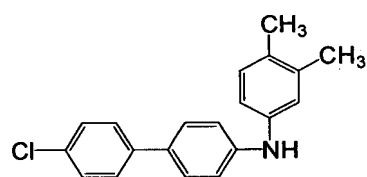
(3-7)



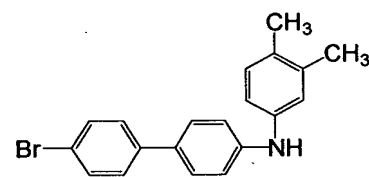
(3-8)



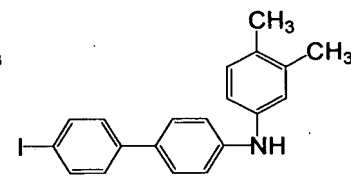
(3-9)



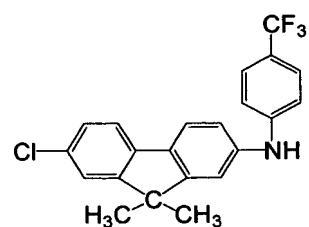
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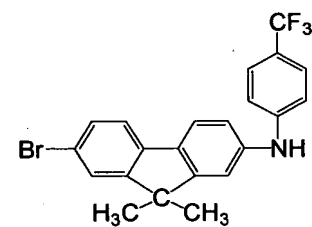
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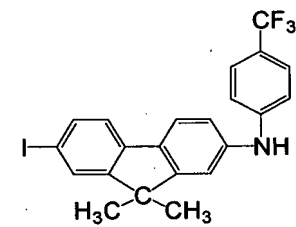
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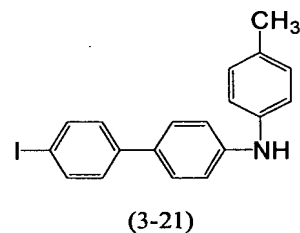
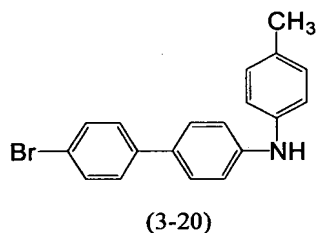
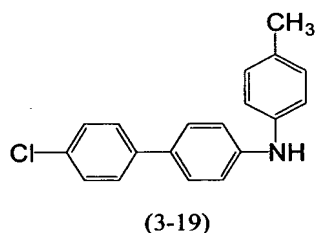
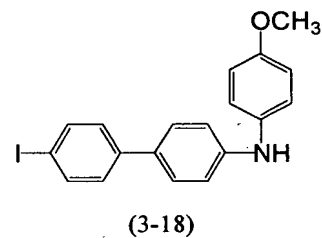
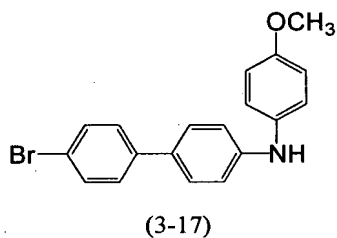
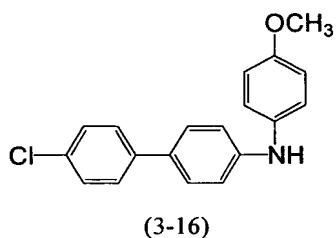
(3-13)



(3-14)



(3-15)



The metallic catalyst in the present invention may preferably be a palladium complex the center-forming metal atom of which is constituted of palladium or a nickel complex the center-forming metal atom of which is constituted of nickel. It may more preferably be a palladium complex constituting of palladium.

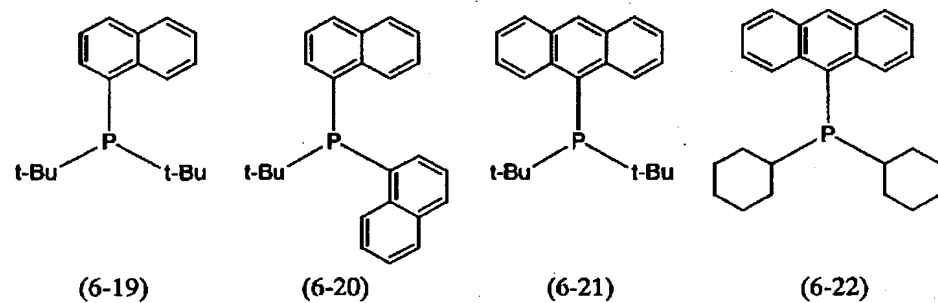
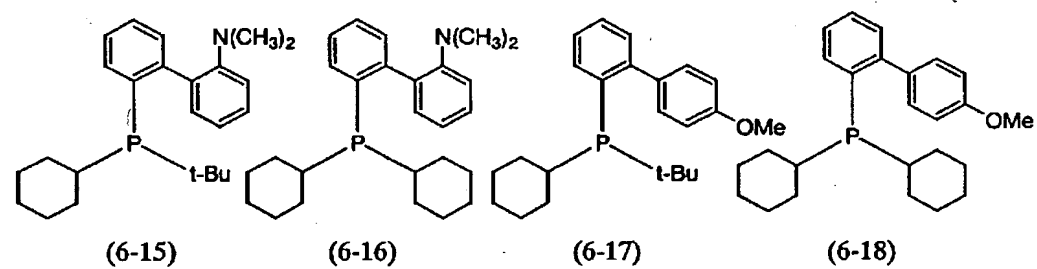
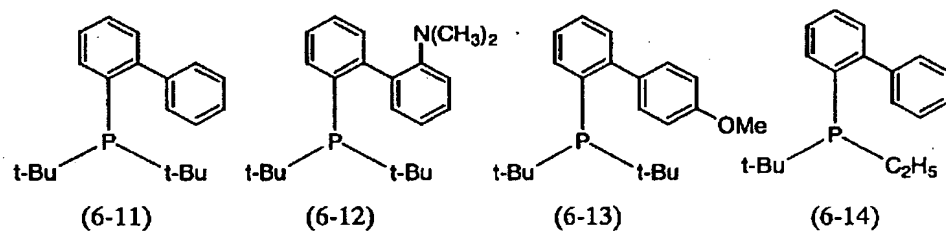
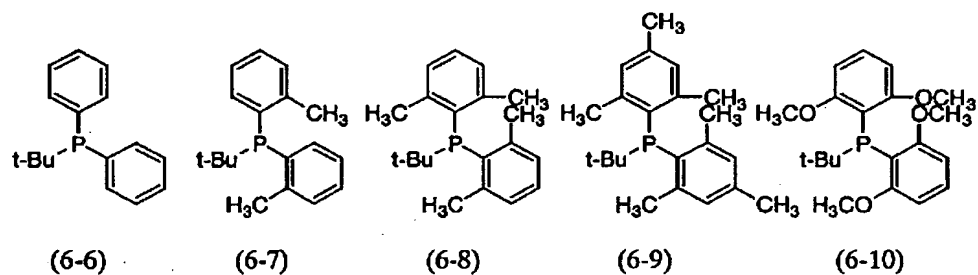
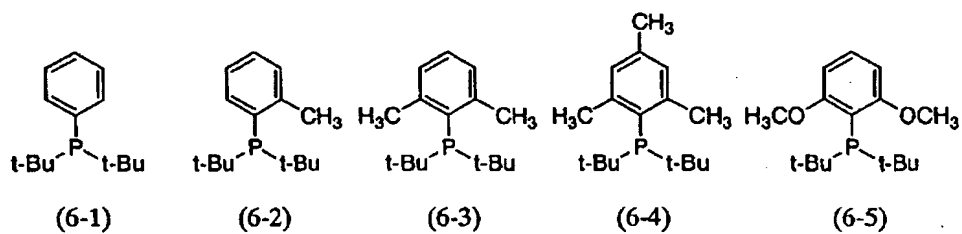
The metallic catalyst which acts on synthesis reaction may be either of a case in which it has already been prepared from a phosphorus-containing ligand and a metal outside the reaction system and a case in which a metallic catalyst having catalytic action is generated by making a metallic compound and a phosphorus-containing ligand present together inside the reaction system. In the latter case, the metallic compound may preferably be a palladium compound or a nickel compound, and may more preferably be a palladium compound, or a nickel compound, selected

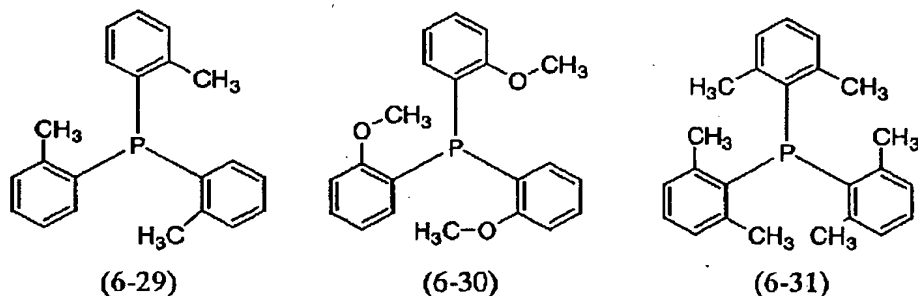
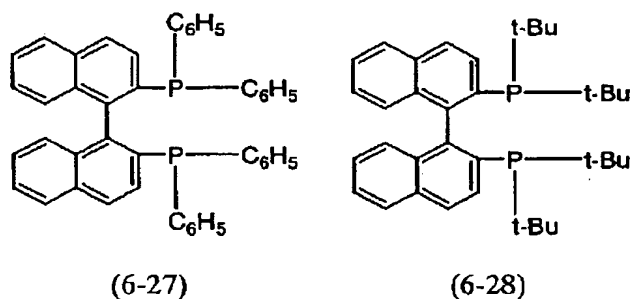
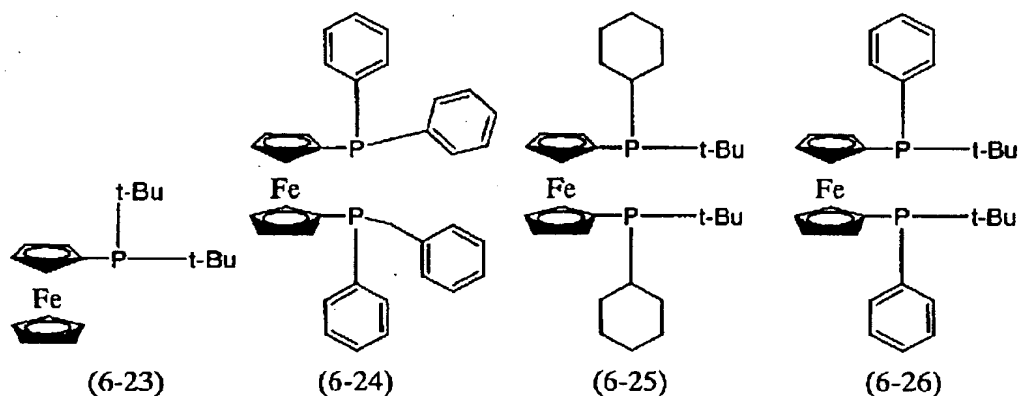
from the group consisting of $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{Aca})_2$,
 $(\text{CH}_3\text{CN})_2\text{Pd}(\text{NO}_2)\text{Cl}$, $(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{PdCl}_2$, $\text{Pd}_2(\text{dba})_3$, PdCl_2 ,
 $\text{Ni}(\text{OAc})_2$, $\text{Ni}(\text{Aca})_2$, $(\text{CH}_3\text{CN})_2\text{Ni}(\text{NO}_2)\text{Cl}$, $(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{NiCl}_2$,
 $\text{Ni}_2(\text{dba})_3$ and NiCl_2 .

5 The metallic catalyst may be used in an amount,
but not particularly limited to, of from 0.0001 to 0.1
mole% in terms of the weight of the metallic catalyst,
and more preferably from 0.002 to 0.08 mole% in terms
of the weight of the metallic catalyst, based on the
10 aromatic amine compound represented by Formula (1).

 The phosphorus-containing ligand in the
production process of the present invention may also
preferably have at least one cyclic hydrocarbon group
on a substituent on the phosphorus. The cyclic
15 hydrocarbon group may also preferably be a substituted
or unsubstituted phenyl group, a substituted or
unsubstituted biphenyl group, a substituted or
unsubstituted naphthyl group or a substituted or
unsubstituted cyclopentadienyl group.

20 Specific structural examples of the
phosphorus-containing ligand are shown below, but not
particularly limited to these. In the following,
"t-Bu" in structural examples represents tert-butyl.





In regard to the amount in which the phosphorus compound is used, it may be, but not particularly limited to, 0.5 time to 10 times in number of moles, based on the metal in the catalyst, and more preferably 0.8 time to 5 times based on the metal in the catalyst.

The basic compound used in the present invention may preferably be a basic compound selected from the group consisting of an alkali metal alkoxide, an

alkaline earth metal alkoxide, potassium carbonate and potassium tertiary phosphate. As examples of the alkali metal alkoxide, it may include lithium methoxide, sodium methoxide, potassium methoxide, 5 lithium ethoxide, sodium ethoxide, potassium ethoxide, lithium isopropoxide, sodium isopropoxide, potassium isopropoxide, lithium tert-butoxide, sodium tert-butoxide and potassium tert-butoxide. As examples of the alkaline earth metal alkoxide, it may include 10 magnesium di(methoxide), magnesium di(ethoxide), magnesium di(isopropoxide) and magnesium di(potassium tert-butoxide).

As the solvent used in the present invention, there are no particular limitations as long as it is a 15 non-reactive solvent that does not participate in the reaction of the present invention, like a halogen solvent. It may preferably be an aromatic hydrocarbon solvent such as benzene, toluene or xylene, or an ether type solvent such as monoglyme, diglyme, 20 tetrahydrofuran or 1,4-dioxane.

In the present invention, the desired compound may be produced under normal pressure in air. In some cases, it may be produced in an atmosphere of inert gas such as nitrogen or argon. Still in some cases, 25 reaction under pressure is feasible. At the time of production, the reaction may be carried out at a temperature between 50°C and 200°C. From the viewpoint

of selectivity, it may be carried out at a temperature of from 50°C to 150°C. Reaction time may differ depending on the type and amount of raw materials used in the production, the type and amount of the metallic catalyst used, the type and amount of the phosphorus-containing ligand used, the type and amount of the basic compound used, the type of the solvent, and the reaction temperature. It may be selected within the range of from few minutes to 120 hours.

10 From the viewpoint of selectivity, it is preferable for the reaction time to be as short as possible.

After the reaction has been completed, the reaction product may be treated by a conventional method to obtain the desired compound.

15 The present invention is described below by giving Examples. The present invention is by no means limited to these.

Example 1

Into a three-necked flask of 200 ml. in inner volume and fitted with a Dimroth type condenser, a thermometer and a stirrer, as an aromatic amine compound 4.65 g (0.05 mol) of aniline, represented by the above Formula (1-25), as a dihalogenated aromatic compound 15.6 g (0.05 mol) of

20 1-bromo-4-(4-bromophenyl)benzene, represented by the above Formula (2-21), as a metallic compound used in a metallic catalyst 20.112 g (0.0005 mol) of Pd(OAc), as

a phosphorus-containing ligand 0.60 g (4 times in number of moles, based on the metal) of the compound represented by Formula (6-11), as a basic compound 5.6 g (0.07 mol) of sodium tert-butoxide, as an internal
5 standard 100 mg of terphenyl and as a solvent 90 ml of toluene were introduced. Thereafter, these were heated in an oil bath to temperature at which the toluene continued reflux, and then stirred for 3 hours to carry out reaction. Thereafter, the reaction mixture
10 was left to cool to room temperature. After the reaction mixture cooled to room temperature, this was neutralized with hydrochloric acid water, and the organic layer was quantitatively analyzed by gas chromatography (HP6890, manufactured by Hewlett
15 Packard Co.) to measure the yield of the desired halogenated aromatic amine compound shown in Table 1. The results are shown in Table 1.

Examples 2 & 3

In Example 1, the aromatic amine compound, the
20 dihalogenated aromatic compound, the metallic compound used in a metallic catalyst and the phosphorus-containing ligand were changed as shown in Table 1, to carry out reaction and quantitative analysis to measure the yield of the desired
25 halogenated aromatic amine compound shown in Table 1. The results are shown in Table 1.

Examples 4 to 6

In Example 1, the aromatic amine compound, the dihalogenated aromatic compound, the metallic compound used in a metallic catalyst and the phosphorus-containing ligand were changed as shown in Table 1 and the solvent was changed to 1,4-dioxane, to carry out reaction and quantitative analysis to measure the yield of the desired halogenated aromatic amine compound shown in Table 1. The results are shown in Table 1.

10 Examples 7 & 8

In Example 1, the aromatic amine compound, the dihalogenated aromatic compound, the metallic compound used in a metallic catalyst and the phosphorus-containing ligand were changed as shown in Table 1 and the solvent was changed to diglyme, to carry out reaction and quantitative analysis to measure the yield of the desired halogenated aromatic amine compound shown in Table 1. The results are shown in Table 1.

20 Comparative Example 1

Into a three-necked flask of 200 ml in inner volume and fitted with a condenser, a thermometer and a stirrer, as an aromatic amine compound 4.65 g (0.05 mol) of aniline, represented by the above Formula (1-25), as a dihalogenated aromatic compound 20.3 g (0.05 mol) of 1-iodo-4-(4-iodophenyl)benzene, represented by the above Formula (2-41), 9.6 g (0.15

mol) of copper powder, as an internal standard 100 mg of terphenyl and as a solvent 90 ml of o-dichlorobenzene were introduced. Thereafter, these were heated in an oil bath to 200°C, and then stirred
5 for 6 hours to carry out reaction. Thereafter, the reaction mixture was left to cool to room temperature. After the reaction mixture cooled to room temperature, the organic layer was quantitatively analyzed by gas chromatography to measure the yield of the halogenated
10 aromatic amine compound shown in Table 1. The results are shown in Table 1.

Comparative Example 2

Into a three-necked flask of 200 ml in inner volume and fitted with a Dimroth type condenser, a
15 thermometer and a stirrer, as an aromatic amine compound 4.65 g (0.05 mol) of aniline, represented by the above Formula (1-25), as a dihalogenated aromatic compound 15.6 g (0.05 mol) of
1-bromo-4-(4-bromophenyl)benzene, represented by the
20 above Formula (2-21), as a metallic compound used in a metallic catalyst 20.112 g (0.0005 mol) of Pd(OAc)₂, as a phosphorus-containing ligand 0.40 g (4 times in number of moles, based on the metal) of
tri(tert-butyl)phosphine, represented by the following
25 Formula (8), as a basic compound 5.6 g (0.07 mol) of sodium tert-butoxide, as an internal standard 100 mg of terphenyl and as a solvent 90 ml of toluene were

introduced. Thereafter, these were heated in an oil bath to temperature at which the toluene continued reflux, and then stirred for 3 hours to carry out reaction. Thereafter, the reaction mixture was left to
5 cool to room temperature. After the reaction mixture cooled to room temperature, this was neutralized with hydrochloric acid water, and the organic layer was quantitatively analyzed by gas chromatography to measure the yield of the halogenated aromatic amine
10 compound shown in Table 1. The results are shown in Table 1.

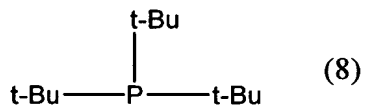


Table 1

	Aromatic amine compound	Dihalo- genated aromatic compound	Metallic compound	Phosphorus= containing ligand	Basic compound	Halogenated aromatic amine compound	Yield
Example:							
1	1-25	2-21	$\text{Pd}(\text{OAc})_2$	6-11	sodium tert-butoxide	3-2	83%
2	1-1	2-51	PdCl_2	6-10	sodium tert-butoxide	3-6	74%
3	1-4	2-23	$\text{Pd}_2(\text{dba})_3$	6-31	sodium tert-butoxide	3-8	78%
4	1-4	2-21	$\text{Pd}(\text{OAc})_2$	6-24	sodium tert-butoxide	3-11	94%
5	1-19	2-31	PdCl_2	6-25	sodium tert-butoxide	3-14	92%
6	1-6	2-41	$\text{Pd}_2(\text{dba})_3$	6-23	sodium tert-butoxide	3-18	84%
7	1-4	2-41	NiCl_2	6-24	sodium tert-butoxide	3-12	78%
8	1-1	2-41	NiCl_2	6-26	sodium tert-butoxide	3-21	72%
Comparative Example:							
1	1-25	2-41	copper powder	-	-	3-3	59%
2	1-25	2-21	$\text{Pd}(\text{OAc})_2$	8	sodium tert-butoxide	3-2	53%

In Examples, the halogenated aminobiphenyl has been obtained in a good yield in all cases. However, in the conventional case Comparative Example 1 (Ullmann process) or in the case when
5 tri(tert-butyl)phosphine is used as the phosphorus-containing ligand, the reaction has a low selectivity, resulting in a low yield of the compound obtained.

As described above, the utility of the present
10 invention has been demonstrated as a process for synthesizing the halogenated aminobiphenyl compound useful as an intermediate of pharmaceuticals and agricultural chemicals, an intermediate of coloring matters such as organic dyes and pigments, and also an
15 intermediate of organoelectroluminescence materials, and an intermediate of photosensitive materials or organic conductor materials of organic photosensitive members in electrophotography.

The present invention makes it possible to
20 provide a production process in which the halogenated aromatic amine compound, which has ever been difficult to produce, is produced in a high selectivity and a high yield from the aromatic amine compound and dihalogenated aromatic compound, by using i) the
25 metallic catalyst having a phosphorus-containing ligand having at least one cyclic hydrocarbon group and ii) the basic compound.